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EXPLOSIVE BEHAVIOR OF DINITROTOLUENE

NOL

10 July 1969

UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

NOLTR 69-92

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EXPLOSIVE BEHAVIOR OF DINITROTOLUENE

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and D. J. Edwards

ABSTRACT: DNT shows Group 1 explosive behavior although it can be dead-pressed moderately easily. Its infinite diameter detonation velocity is approximated by

$$D_1 \text{ (mm/}\mu\text{sec)} = 1.84 + 2.913 \rho_0$$

Its detonability and shock sensitivity are, respectively, near those of high bulk density nitroguanidine and DATB. A review of factors affecting detonability and sensitivity of a chemically homogeneous explosive is also presented.

Published 10 July 1969

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NOLTR 69-92

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EXPLOSIVE BEHAVIOR OF DINITROTOLUENE

This work was carried out under the tasks MAT 03L 000/RO11 01 01 FR 59 and ORDTASK 033 102 F009 06 01. Its results are most useful in contributing to the knowledge of explosive detonability and shock sensitivity.

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EXPLOSIVE BEHAVIOR OF DINITROTOLUENE

INTRODUCTION

In earlier work¹, we quoted a Russian review² which stated that Blinov³ had shown that dinitrotoluene (DNT), dinitrophenol, and other dinitro-compounds of aromatic hydrocarbons exhibit Group 2 explosive behavior, i.e., their critical diameter for detonation increases with increasing loading density (ρ_0). The objective of the present work was to investigate the validity of that reported behavior. The results of our studies of the detonation velocity (D) as a function of ρ_0 and diameter (d), of detonability, and of shock sensitivity are reported here. They show clearly that the explosive behavior of DNT is generally that of Group 1, not Group 2, materials. The erroneous statement in the literature resulted, we believe, from an improper interpretation of experimental observations.

EXPERIMENTAL

The explosive, 2,4-dinitrotoluene, $\text{CH}_3 \cdot \text{C}_6\text{H}_3 \cdot (\text{NO}_2)_2$ has a crystal density of 1.52 g/cc and melts at 70°C⁴. By arbitrary decomposition mechanisms a and b*, on a per gram basis, its heat of detonation is 89-82% that of TNT, and the volume of its gas products is the same. It would be expected to resemble TNT rather closely in its general behavior.

Two lots of 2,4-dinitrotoluene, tech., were obtained from du Pont; they satisfied the du Pont sales specifications of 10/26/65 for this material (97.5% DNT or better). The two lots were given the designations X587 and N137. They had average particle sizes of 150 and 350 μ respectively, and corresponding pour densities of 0.70 and 0.57 g/cc. Sieve analyses are given in the appendix. A portion of lot X587 was used to prepare, by re-crystallization, about 30 pounds of fine (3 to 10 μ) DNT, designated as X628.

Charge preparation and handling were identical to those of previous work.⁵ Charges were of various diameters, 20.32 cm long,

* a. Formation of H_2O , CO_2 in sequence; b. formation of CO , H_2O , CO_2 in sequence.

and boosters were 50/50 pentolite ($\rho_0 = 1.56$ g/cc) of the same diameter and 5.08 cm long. The experimental assembly and instrumentation for detonation velocity measurements (70mm smear camera with writing speed up to 4mm/ μ sec or ionization probes at various stations) were also the same⁵. Record reduction was carried out as in the previous work and, in addition, small corrections⁶ have been made to the optically measured D value.

REVIEW OF RELEVANT PUBLICATIONS

As we stated above, the work of Blinov and his colleagues seems to be the source of the statement that dinitro-compounds of aromatic hydrocarbons exhibit Group 2 behavior. Although we still have not seen Blinov's original publication³, we have obtained the translation of a later work⁷ which claims to show the same results. Also available now is the translation of a second, earlier paper⁸ which is also a study of dinitro aromatics.

In both papers^{7,8} Blinov used the compression (change in height) of a lead cylinder as a measure of "explosiveness." Moreover, in 1959, he states⁸, "...the explosiveness of dinitro compounds usually drops off with increase in bulk density..." The lead cylinder test with no instrumentation, in particular without detonation velocity measurements, is evidently the basis for assuming a trend of increasing critical diameter with increasing density. This is indirect evidence very like that of a plate dent in the gap test. Such evidence has already been shown unreliable for high bulk density nitroguanidine, NQ-h⁹.

Blinov further stated in 1959 that DNT packed in paper cannot be detonated without use of a booster (at least 3g of pressed tetryl). This is for a low density charge, one close to the pour-density of the material. The work was carried out on technical grade materials which passed a No. 30 screen. Similar material was also used for the later work⁷ in which the lead cylinder values of Table 1 were given for various confined charges of DNT at 0.6 and 0.8 g/cc bulk density. Blinov states that they confirm "that the critical diameter of propagation of detonation in it grows with an increase in density." We believe that the data of Table 1 suggest exactly the reverse of his conclusion. (See discussion below)

TABLE 1
Blinov's Values for Lead Cylinder Test of DNT⁷

Casing	Casing diam.		Casing Wt/length g/cm	Decrease in height of Lead cylinder ^a $\Delta h, \text{mm}$	$\Delta h/\rho_0$
	I.D.	O.D.			
$\rho_0 = 0.6 \text{ g/cc}^b$					
1. Steel with seam	40	48	38	16.1	26.8
2. Steel with seam + slit	40	48	38	12.8	21.3
3. Lead	40	44	30	21.3	35.4 ^c
4. H ₂ O	40	80	40	13.7, 15.0	22.8, 25.0
5. Clay	40	64	40	17.0, 14.6	28.3, 24.3
6. Tin	40	41.2	3	15.2, 15.6	25.3, 26.0
$\rho_0 = 0.8 \text{ g/cc}$					
1. Steel with seam	40	48	40	26.4	33.0 ^c
2. Steel with seam + slit	40	48	40	25.0	31.2 ^c
3. Lead	40	46	40	26.0	32.5 ^c
4. H ₂ O	40	80	40	1.2, 1.2	1.5, 1.5
5. Clay	40	64	40	1.5	1.9
6. Tin	40	41.2	7	1.0, 0.8	1.3, 1.0

a. Charges initiated with No. 8 cap, no booster use. Charge length 100 mm. When a 10 g tetryl booster was used against an inert (hexamethylenetetramine at unspecified density), the control result was 9mm.

b. At this density, d_c of unconfined charge was reported as 45mm. On comparable material at 0.7 g/cc we found $d_c > 76\text{mm}$.

c. Detonation may have occurred.

Our technical grade DNT (X587) had a pour-density of about 0.7 g/cc and the sieve analysis shown in the appendix. In large diameters (6.3 or 7.6cm) a standard pentolite donor initiated reaction for unconfined charges $0.7 \leq \rho_0 \leq 1.33$ g/cc, but the front velocity decreased as it propagated and was not a detonation. At $\rho_0 = 0.7$ g/cc the front velocity seemed nearly constant and at $\rho_0 = 1.5$ g/cc no reaction was initiated. In the gap test confinement, charges at $\rho_0 = 1.0$ and $\rho_0 = 1.5$ g/cc did detonate. In order to obtain detonation of smaller diameter unconfined charges, it was necessary to use a fine ($\sim 10\mu$) DNT.

It is quite easy to initiate non-steady state reactions in granular charges of coarse materials and such reactions, as we have shown for NQ-h, are powerful enough to punch or dent a steel witness plate (or flatten a lead cylinder). It is such reactions that are probably responsible for most of the lead cylinder results of Table 1. These show that the output increases with ρ_0 for strong confinement, but shows the reverse trend for weak confinement. Only the four results marked with a (c) seem to be possible detonations, and, if so, these show that the higher density favors detonability or that the d_c decreases as ρ_0 increases.

Finally, in yet another paper¹⁰, Blinov comments again that he had previously established an increase in critical diameter with an increase in loading density for the dinitro-compounds. But he adds, "At the same time, upon lowering of density, failures are observed with those methods of initiation that ensure explosion of charges of large density." However, his results were confused by using essentially point initiation (both boosted and unboosted) on large diameter, shock insensitive materials. Most of the lead cylinder results on the weakly confined charges in Table 1 seem best explained as caused by a sub-detonation, reactive shock, possibly in many cases at effective diameters below the critical diameter for detonation. The opposite trends (with density) found for such a reactive shock as compared to true detonation are analogous to those demonstrated for NQ-h.⁹

PRESENT RESULTS

Detonation Velocity.

Because it was impossible to initiate detonation* of the unconfined coarse DNT (X587) in charges small enough to handle conveniently in our firing facilities, we obtained a batch of very fine DNT (I623) to use for most of the optical work. The velocity measurements are listed in Table 2. Fig. 1 shows the extrapolation of the D vs d^{-1} data to infinite diameter for the loading densities of 1.507 g/cc and 1.301 g/cc (two point extrapolation only). This gives the two D_1 values shown in Table 2. If a linear D_1 vs ρ_0 is also assumed, these data give

$$D_1(\text{mm}/\mu\text{sec}) = 1.84 + 2.913 \rho_0 \quad (1)$$

as the infinite diameter relationship for DNT. We realize that Eq. (1) could be far better established with a larger number of determinations, but our supply of fine DNT was limited. Eq. (1) is adequate as a guide to the $D = D(\rho_0, d)$ pattern of DNT and seems to be the only D_1 vs ρ_0 curve available for this material. Moreover, it is supported by some measurements carried out on confined and internally boosted coarse DNT, as will be shown. Fig. 2 shows the $D = D(\rho_0, d)$ pattern for DNT. It is a normal Group 1 pattern.

Confinement should increase the detonability (decrease the critical diameter) of coarse DNT. To assess this effect, probe measurements were made on confined coarse DNT, X587; they are given in Table 3. This lot of DNT in the gap test confinement exhibits D values very close to those of the fine DNT detonating unconfined in 7.62 cm diameter charges (see Table 2); it is certainly detonating.

* As noted above, however, it was very easy to initiate a vigorous reaction with the donor shock. For $d = 7.62$ cm, $\rho_0 = 0.70$ to 1.39 g/cc, reaction fronts of slowly decreasing velocities of about 2.36 to 4.77 mm/ μ sec were observed. At $\rho_0 = 1.50$ g/cc or $d = 5.1$ cm, failure was much more rapid.

TABLE 2
Detonation Velocity Measurements on Fine DNT, X628

Shot No.	ρ_0 g/cc	d cm	D mm/ μ sec	D_1	D_2
567	1.302H	3.81	4.722	4.704	4.708
522	1.301H	5.08	5.120	5.075	5.081
569	1.301H	7.62	5.333	5.252	5.266
$D_1(1.301\text{g/cc}) = 5.63\text{mm}/\mu\text{sec}$					
552	1.5061	2.54	5.395	5.386	5.387
566	1.5071	3.495	5.700	5.681	5.684
548	1.5111	5.08	5.864	5.798	5.802
568	1.4951	7.62	6.032	5.983	5.993
$D_1(1.507\text{g/cc}) = 6.23\text{mm}/\mu\text{sec}$					
518	1.001h	5.08	F	F	F
530	1.157H	↓	3.751	3.718	3.726
577	1.226H		4.685	4.653	4.660
531	1.408H		5.512*	5.464	5.468
548	1.5111		5.864	5.812	5.816
523	1.001h	7.62	3.590	3.520	3.542

* Trace over-exposed; reading made on sharper edge.

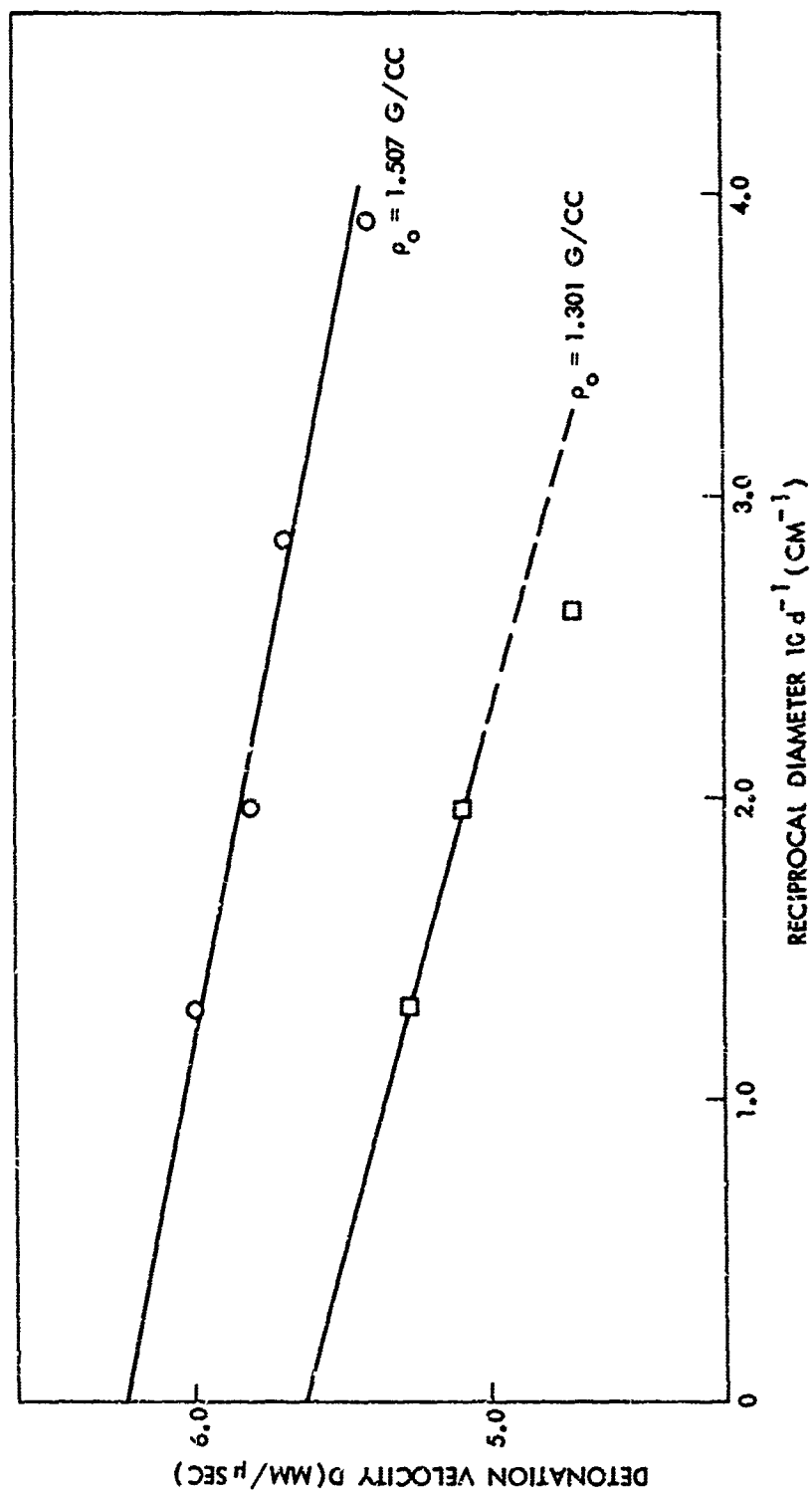


FIG. 1 DIAMETER EFFECT ON DETONATION VELOCITY OF DNT, X628

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TABLE 3

D Measurements by Probes on Coarse DNT, X587*

<u>Shct No.</u>	<u>ρ_0 g/cc</u>	<u>D mm/μsec</u>	<u>σ</u>
1	1.00	3.788	0.013
2	1.00	3.772	0.037
3	1.50	Failed	
4	1.50	5.908	0.051

*Charges confined in 12 in. length of standard gap test tubing bored to take probes. Detailed measurements given in Appendix.

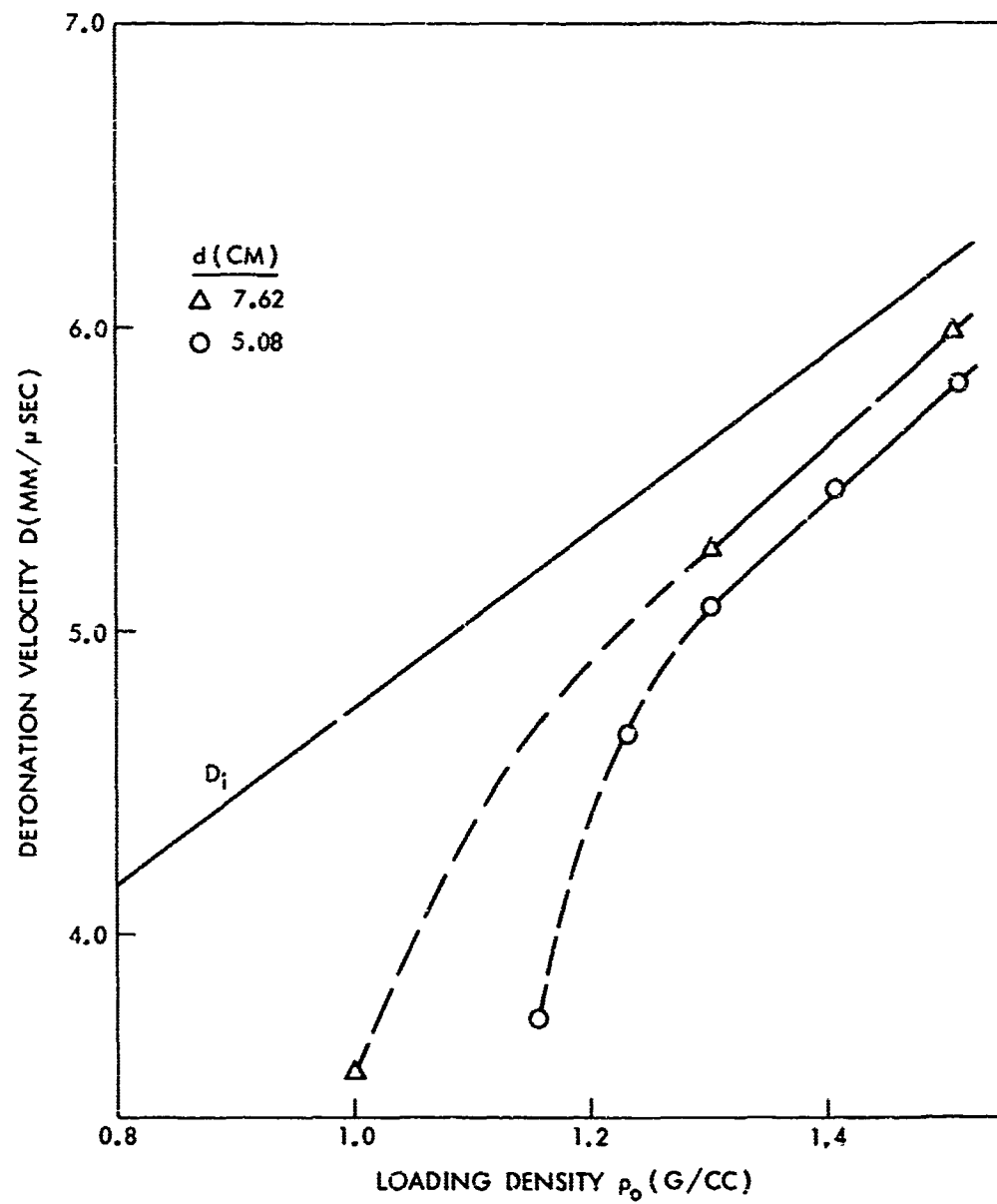


FIG. 2 PATTERN OF D VS. ρ_0 CURVES FOR DNT AT TWO DIFFERENT CHARGE DIAMETERS

This increase in the effective diameter by confinement is important⁷ because of the conditional relationship between d_c at P_g , i.e., only for $d \geq d_c$ can detonation be achieved and hence a sensitivity (P_g) to shock-to-detonation transition measured. Because this condition is satisfied for coarse DNT in the range 1.0 to 1.5 g/cc and in the gap test confinement, meaningful shock sensitivity measurements (P_g) can be made. (The particle size effect on shock sensitivity is small compared to its effect on critical diameter.) Finally, the failure of shot 3 (Table 3) at $\rho_0 = 1.50$ g/cc suggests the possibility that dead pressing occurs in this material.

Another check of the detonation pattern of Fig. 2 and of the ideal curve, Eq. (1), was made on an 80/20 mixture of DNT/RDX. The DNT was coarse (X587); the RDX, medium fine (Type B, Class A). The results, detonation velocity as a function of charge diameter, are given in Table 4 and plotted in Fig. 3 which also shows the extrapolation to the infinite diameter value D_1 of the mixture. Since the charges were of low porosity (99.2% TMD), the additivity rule for H.E. mixtures should be applicable. It gives for pure DNT, $D_1 = 6.25$ mm/ μ sec at $\rho_0 = 1.5075$ g/cc. At the same density Eq. (1) predicts 6.23 mm/ μ sec which is an excellent check.

Detonability

Table 2 contains the velocities measured on charges of fine DNT which detonated. Table 5 presents the failures that were observed and summarizes the failure limit data obtained by combining the results of both tables. Fig. 4 is a plot of the resultant detonability curve. It lies somewhat above and to the right of the limit curve for NQ-h⁹ and far below and to the left of the limit curve of the coarse DNT, X587. Over most of the %TMD range, the fine DNT has a greater d_c than does NQ-h, but the two curves cross at 87% TMD. At and above 87% TMD, therefore, the NQ-h has a greater d_c than DNT. It should be noted, however, that the NQ-h and DNT X587 are about comparable in particle size (ca. 100-150 μ) whereas, the fine DNT consists of 3-10 μ particles. It can be concluded that the propagation of detonation is much more difficult in DNT than in any of the other H.E. studied except NQ-h.

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TABLE 4

Detonation Velocity of DNT/RDX, 80/20

<u>Shot No.</u>	<u>ρ_0^* g/cc</u>	<u>d cm</u>	<u>D mm/μsec</u>	<u>D₁</u>	<u>D₂</u>
559	1.560	2.54	5.934	5.924	5.924
560	1.558	3.495	6.573	6.552	6.552
561	1.556	5.08	6.699	6.653	6.654
562	1.554	7.62	6.751	6.648	6.651

$D_1 = 6.75 \text{ mm}/\mu\text{sec at } \rho_0 = 1.556 \text{ g/cc}$
(99.18%TMD)

* $\rho_v = 1.569 \text{ g/cc}$

Coarse DNT, X587

Medium RDX, X597 (Type B, Class A)

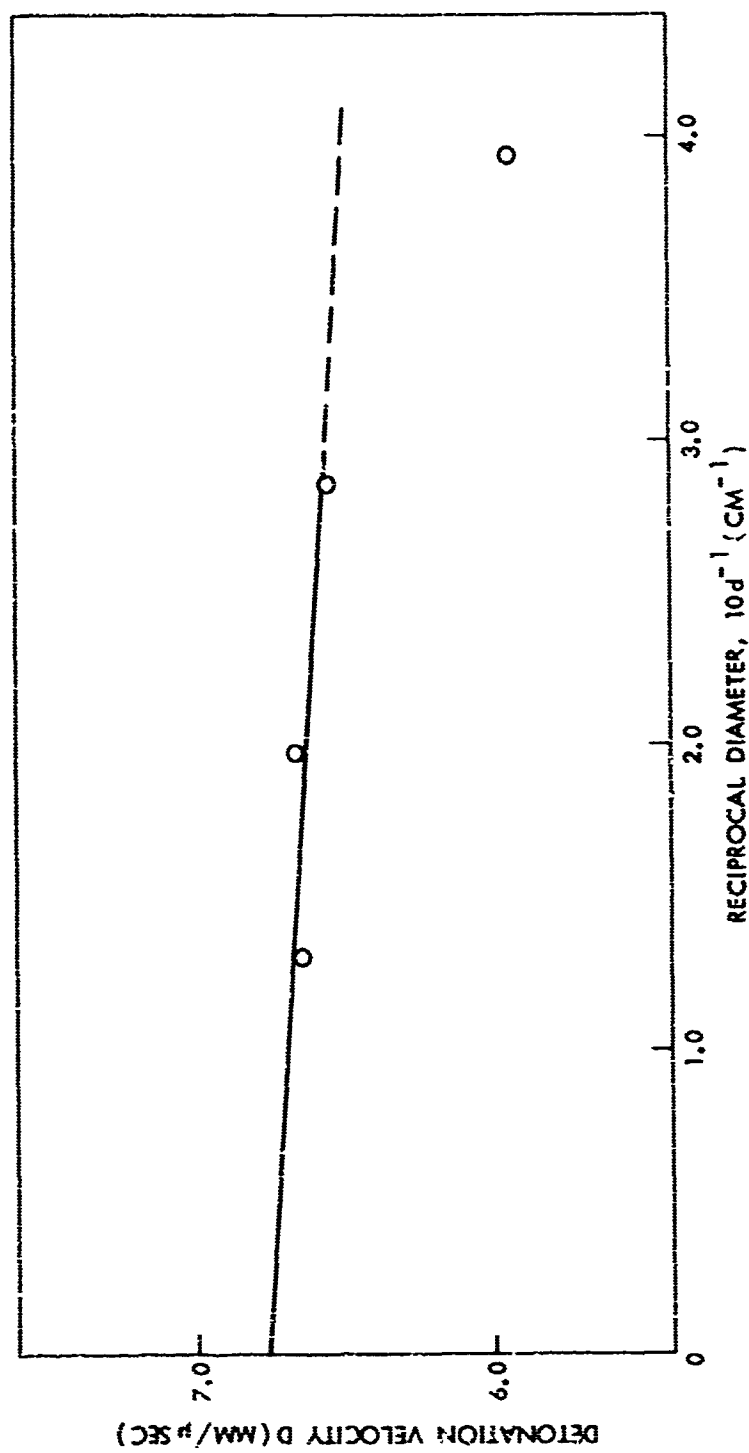


FIG. 3 D VS. d^{-1} CUP'E FOR DNT/RDX, 80/20, AT 99.18% TMD

TABLE 5
Failures Observed on Fine DNT, X628

Shot No.	d cm	ρ_0 g/cc	Failure at δ cm
518	5.08	1.001h	15.2
511	2.54	0.800h ^a	5.7
506		1.001h ^a	15.2 ^b
512		1.204h	6.6 ^b
513		1.406h	9.9 ^d
582		1.514i ^e	<10.2 ^d
573	1.97	1.507i ^e	<7.9 ^d

Summary of Detonability Data (Tables 2 and 5)

ρ_0 g/cc	d_+ cm	d_- cm
1.00	7.62	5.08
1.16	5.08*	2.54
1.30	3.81*	2.54
1.40	5.08	2.54
1.506	2.54	--
1.514	--	2.54

* Record suggests this is very near d_c .

- a. Preliminary laboratory sample of 10-15 μ DNT used.
- b. Booster only 2.54 cm long, by error.
- c. Shavings from previous charges used.
- d. No trace on record; unreacted DNT recovered.

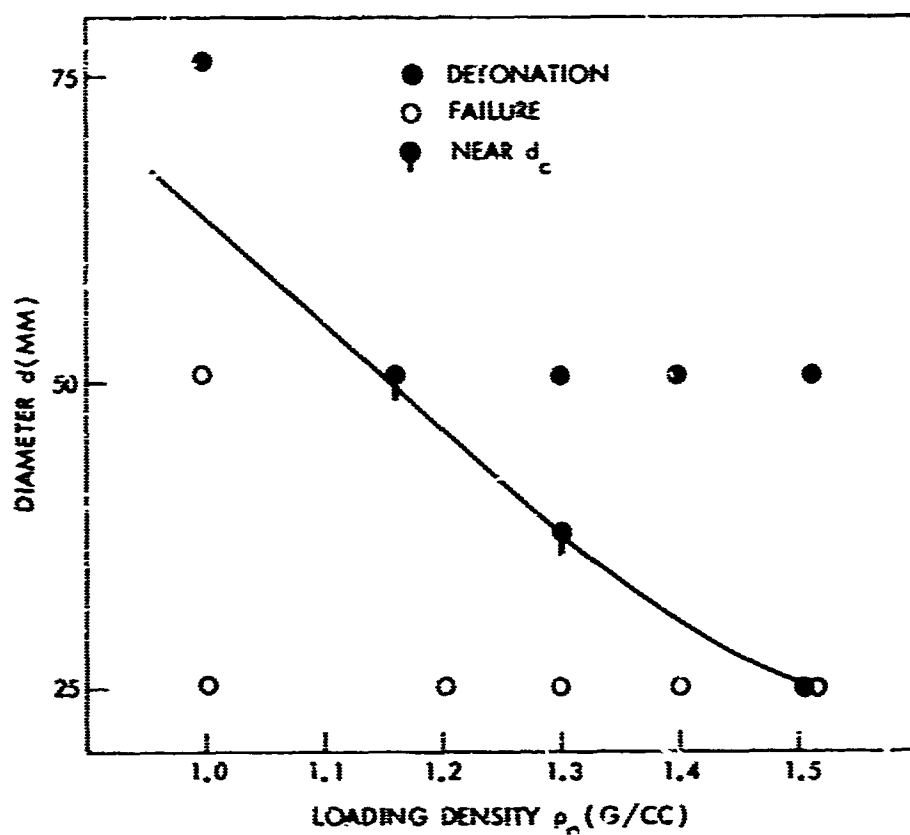


FIG. 4 DETONABILITY CURVE OF 3-10 μ DNT, X628

NQ-h shows a definite reversal of its detonability curve at higher densities, a dead press phenomenon.⁹ The limit curve of Fig. 4 only suggests this possibility for DNT by its curvature near the crystal density. The two failures observed at $\rho_0 \geq 1.507$ g/cc (Table 5) also indicate the possibility as does the one failure of coarse DNT at 1.5 g/cc (Table 3). Subsequent work in the gap test configuration confirmed the fact that DNT does exhibit dead pressing although not as readily as NQ-h.

The trend of Fig. 4 is definitely that of a Group 1 material as would be expected from the $D(\rho_0, d)$ pattern of Fig. 2. Nevertheless, it seems likely for the reasons given above, that DNT in some particle size distribution and state of compaction will exhibit a reversal in its detonability similar to that shown by NQ-h. On the high density branch of the limit curve, it would be expected to show a Group 2 (e.g., ammonium perchlorate) behavior pattern. It should be noted that the present fine DNT has a d_c comparable to that of fine AP's in the 70 to 75 percent TMD range. Table 6 compares the present results for fine DNT with NQ-h, AP's, DATB, and TATB.

Shock Sensitivity

Shock sensitivity was studied on coarse DNT because the fine DNT was available only in limited supply. However, the work on nitroguanidine⁹ showed that the particle size effect on shock sensitivity is small (particularly as compared to the effect on critical diameter) provided that the test material is detonating and not undergoing a vigorous but subdetonation reaction. Moreover, the shock sensitivity curves (P_g vs ρ_0) of the fine and coarse NQ approach each other as ρ_0 increases.

Table 7 contains the few gap test results on coarse DNT, lot X587. The very high P_g required to initiate the 98.9 percent TMD charge indicates that dead pressing should occur at some %TMD >98.9% (that limit was the highest compaction of the coarse material that we could obtain in our press). Of course, the fact that cast DNT could not be initiated to detonation in the same configuration (See Table 7) strengthens the expectation that dead pressing will occur at some high compaction.

TABLE 6
Comparison of d_c of DNT, X628 with That of Similar H.E.

Material	Ref.	%TMD:	Critical Diameter for Detonation d _c (mm)					
			70	75	80	85	90	98
DNT (10μ)		58	51.5	44.5	38	31.5	28	25
NQ-h (~100μ)	9	49	41.5	36.5	35	36.5	>37	>37
DATB (fine)	11	--	--	--	--	--	--	5.3
TATB (fine)	11	--	--	--	--	--	13	--
AP (10μ)	5	29.5	47	72	>76	>76	>76	>76
AP (25μ)	5	45	60	>76	>76	>76	>76	>76

TABLE 7
Shock Sensitivity Tests on DNT, X537

<u>P₀</u> <u>g/gg</u>	<u>%</u> <u>TMD</u>	<u>Gap Test</u> <u>Extended/Regular</u> <u>No. Cards</u>	<u>P₀</u> <u>kg/cm²</u>	<u>Comment</u>
0.704h	46.3	~190	--	In view of D(p ₀ ,d) pattern material probably not detonating.
0.999h	65.9	181	21.3	Probably near failure limit.
1.5021	98.9	24	105	Near dead press limit.
1.453	0.4nt	12*	Neg.	Definitely not detonating.

* Result negative with double length tube

After lot X587 of the coarse DNT was exhausted, lot N137, a somewhat coarser DNT was obtained. Gap test results on this material are given in Table 8. Surprisingly, it was impossible to compact this material to a dead-press density (in the gap test) or even to as insensitive a state as was achieved with lot X587. However, the shots made at smaller diameter (data at bottom of Table 8) show that if the acceptor and its confinement were scaled to 0.7 the standard test dimensions, dead pressing occurred between 93 and 97 percent TMD.

In the region 79-98% TMD, the regular gap test results gave a normal sensitivity curve for this material: P_g increases with increasing %TMD. The curve is shown in Fig. 5 where it is compared to sensitivity curves for NQ-h, TATB, DATB, and TNT. (References for these curves are given in Table 9.) All of these materials except TNT give negative results on the impact test^{8,9,11}, i.e., they are difficult to ignite even in powder form. In the LSGT, there is increasing difficulty of ignition under shock in the order TNT, DATB, DNT, TATB, and NQ-h. The last is by far the most difficult to ignite and exhibits dead pressing in the regular gap test (with consequent reversal of its detonability curves) in the higher range of % TMD. We have not been able to demonstrate that any of the other Group 1 explosives will show this phenomenon in the regular gap test although DNT, X587, and TATB seem to be headed toward dead-pressing at 100% TMD.

The two dashed curves of Fig. 5, for TATB and DATB, have been derived from small scale gap test (SSGT) data and their correlation with the LSGT data described in previous work¹². Testing the shock sensitivity of DNT to detonation in the SSGT is impossible. NQ-h will not detonate in the SSGT^{9,12}, and DNT has a critical diameter which is, over most of the % TMD range, even larger than that of NQ-h. Hence DNT is subcritical in the SSGT.

The dotted portion of the TATB curve in Fig. 5 is for the region of % TMD > 95% where a good correlation does not exist between the LSGT and SSGT results. A sharp increase in gradient of the LSGT shock sensitivity curve has been found only for NQ-h⁹, AP¹⁴, and AP mixtures¹⁴, and in each case it signals the occurrence of dead-pressing. On the other hand, it occurs commonly in the SSGT shock

TABLE 8
Shock Sensitivity Tests on DNT, N137

P_o g/cc	% TMD	No. Cards	P_g (kbars)	Regular Gap Test	Comment
1.100H	72.3	143	33.3		Reversal of trend and fact that N137 is coarser than X587 suggests that this charge was not detonating.
1.203H	79.1	144	32.5		
1.271H	83.7	137	35.4		
1.397H	91.8	115	43.7		
1.4921	98.1	85	55.9		
Zero Gap, Regular Test					
1.5071	99.1	Positive			Double length tube.
1.5151	99.7	"			This material cannot be dead pressed in dimensions of regular gap test.
1.5181	99.9	"			
Zero Gap, Regular test with acceptor scaled to 0.70					
1.3151	86.5	Positive			Material does dead press at 0.7 scale of regular test.
1.3571	89.3	"			
1.4071	92.6	"			
1.4701	96.7	Negative			

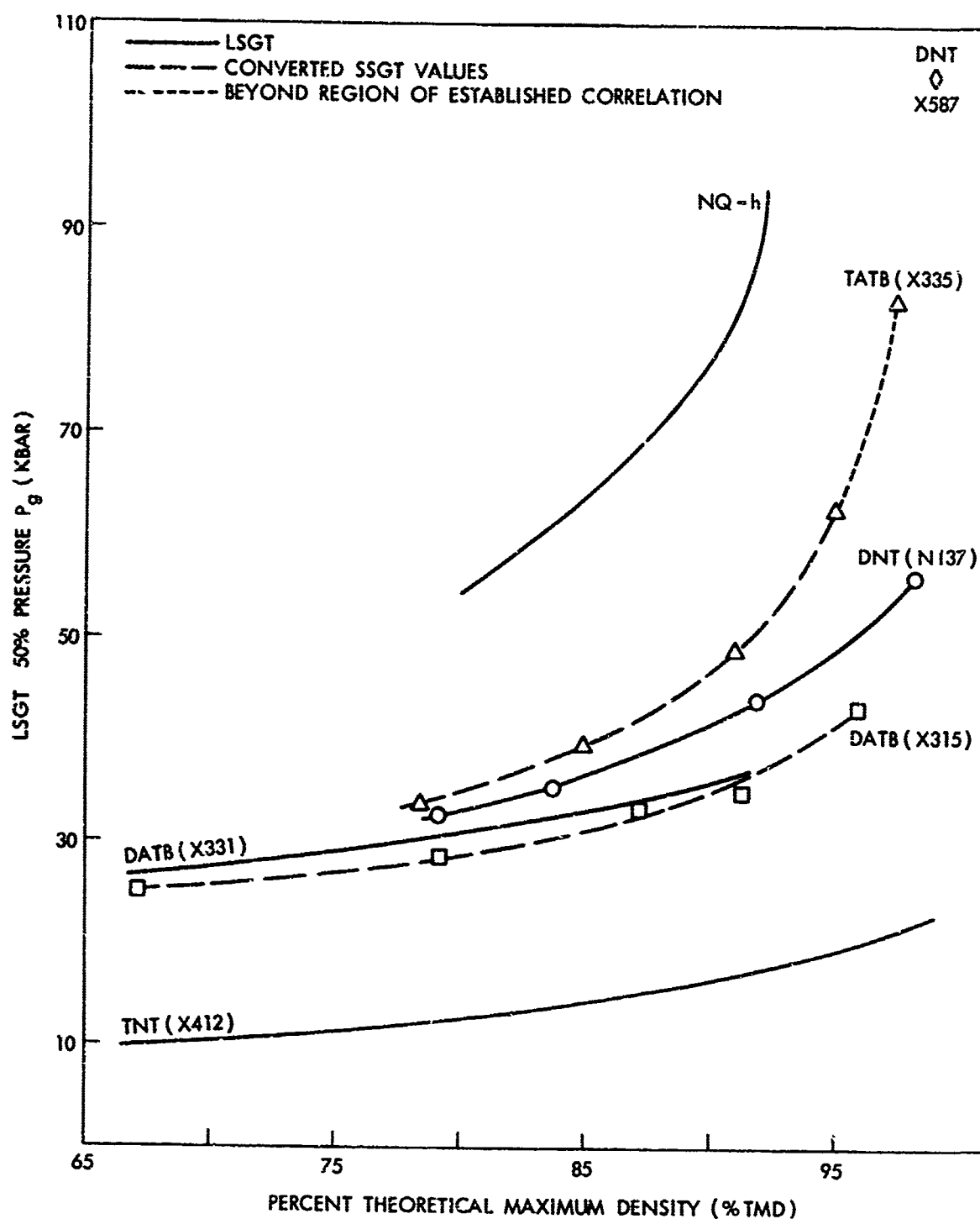


FIG. 5 COMPARISON OF SHOCK SENSITIVITY OF DNT WITH THAT OF SOME OTHER EXPLOSIVES

TABLE 9

Source of Comparative Shock Sensitivity Curves of Fig. 5

<u>Material</u>	<u>Reference</u>	<u>Comment</u>
NQ-h	9	Average particle size up to 100 μ
DATB, X331	12	" " " 50-100 μ , production lot
TNT, X412	12	
TATB, X406	12	
TATB, X335	13	
DATB, X315	13	" " " 50-100 μ , production lot

CONVERSION OF SSGT VALUES TO LSGT VALUES¹²

<u>ρ_0(g/cc)</u>	<u>%TMD</u>	<u>50% Point</u>		
		<u>DBG</u>	<u>SSGT, P (kbar) g</u>	<u>LSGT, P (kbar) g</u>
DATB, X315				
1.233	67.12	6.94	31.2	25.0
1.455	79.20	7.38	35.8	28.5
1.601	87.15	7.88	42.2	33.2
1.676	91.24	8.10	45.3	34.8
1.761	95.86	9.00	60.8	43.2
TATB, X335*				
1.519	78.38	7.92	43.2	33.7
1.645	84.88	8.56	52.5	39.3
1.762	90.92	9.63	74.1	48.8
1.840	94.94	11.10	117.5	62.5
1.887	97.37	13.47	162.2	83.0

* Data for TATB, X406 of Reference 12 give almost coincident curve. Particle size of these lots is unknown.

sensitivity curves¹². The similarity suggests that many materials are approaching a dead press limit near 100% TMD in the SSGT. Difference in the location of such a limit in the two cases probably arises from the difference in the value of the ratio of the effective test diameter to the critical diameter (larger for the LSGT) and the lesser insulation of hot spot areas in the smaller test. Ignition at low porosity will be equally difficult in both cases, but propagation of either burning or detonation should be more difficult in the smaller test.

Finally it should be mentioned that the chemical energy released by decomposition must have a role in affecting both ease of ignition and propagation although it alone is insufficient to determine shock sensitivity ordering. The shock sensitivities shown in Fig. 5 are in the same approximate order as the computed energy release in detonation, but fine AP (with a lower chemical energy than any of them) ranges in shock sensitivity from that of DATB to less than that of NQ-h, depending on its % TMD.

GENERAL CONSIDERATIONS OF SHOCK SENSITIVITY AND DETONABILITY

Every study, such as that of the present report, contributes something to our general knowledge of the shock sensitivity and detonability of explosives. It is therefore appropriate to give here a brief revised summary of our present view of the whole field.

The variable, % TMD, is related to the percent porosity or $(100 - \% \text{ TMD})$. Hence it is a relative measure of internal surfaces available for ignition and reaction. It is only relative because a different particle size distribution will give different size voids and a different sensitivity curve. But, as we have pointed out before, the difference in P_g is not very large and two curves, corresponding to two different particle size distributions, tend to become coincident at high compaction (high % TMD). Hence the trend of the usual shock sensitivity curve P_g vs % TMD, shows that ignition by shock becomes more difficult as the amount of internal surface decreases. For any series of cold pressed charges, % TMD is a valuable guide to both shock sensitivity (P_g) and detonability (d_c). There seems to be some relationship between P_g and d_c within any given

cold-pressed series, but it must be a very limited one. Change of explosive particle size effects a very large change in d_c and only a moderate one in P_g . Moreover, the trends of P_g and d_c with % TMD are opposite for Group 1 explosives and the same for Group 2 explosives. Consequently, there is no evidence of a general relationship between P_g and d_c for pressed charges, and, as we shall show below, very little evidence of one for more homogeneous explosives.

Another way (besides compaction) of decreasing internal surface or changing its reactivity or both is by changing charge preparation. Thus for castable explosives, charges which are pressed, hot pressed, cast, and single crystal, respectively, range from relatively large to near zero internal surface. In such a series of charges with a high (96-100) % TMD, density or % TMD is no longer useful in predicting either P_g or d_c . Instead, the dominant factor seems to be the extent to which the charge approximates perfect physical homogeneity (a perfect single crystal). Both P_g and d_c show large increases as true homogeneity is approached.

The two cases: (a) clearly heterogeneous, porous, granular charges (%TMD dominant factor and particle size distribution a secondary factor) and (b) an approximately homogeneous state (degree of homogeneity dominant factor) can best be illustrated with TNT data. For case (a), the P_g vs % TMD trend is that shown in Fig. 5 with maximum P_g of 23 kbar at 99% TMD. But seven typical cast charges of TNT ranged from 26-46 kbar in P_g and one cast TNT, prepared by very slow cooling of the mold, was off-scale because it could not be initiated to detonation in the gap test. These cast charges were all high density (96-98% TMD) and indistinguishable by this variable. The large effect of the cooling schedule indicates that here homogeneity, especially as affected by grain size, is the dominant factor in determining ignitability under shock (P_g). Hence cast TNT falls under case (b) above.*

* It seems reasonable to consider a major difference between pressed and cast TNT (at the same density) as many and uniformly distributed small voids compared to few and randomly distributed larger voids. A second difference, when the cast material closely approximates homogeneity, is small crystals in the pressed and large crystals in the cast TNT.

The qualitative interpretation of these data seems straightforward. For case (a) ignition is a surface phenomenon controlled by the number of hot spots formed under shock. These in turn depend on the porosity (measured by % TMD), number and shape of voids, amount of internal surface and its reactivity. For case (b), at its extreme of a perfect crystal, there is no internal surface, and ignition (thermal explosion) must occur within homogeneous material as a result of bulk heating caused by shock compression. This seems the only shock ignition mechanism for completely homogeneous explosives, and the data on approximately homogeneous (cast) TNT suggest that it is the dominant factor in the approximately homogeneous region of case (b).

For completeness it should be noted that although the approximate homogeneity of case (b) has been obtained by the method of charge preparation (e.g., a casting or forming a single crystal instead of compacting small crystals), it is also obtained by extending the range of compaction. Thus, both castable and non-castable explosives can be made non-detonable (in given dimensions) by dynamic precompression to 105% or 110% TMD¹⁵. A major effect of such preliminary shocking of compacted charges would be to squeeze out all internal voids and eliminate internal surfaces where hot spots could form. In other words, the precompressed material would have to be ignited by bulk compression heating or not at all.

To cover both cases (a) and (b), we need an ignition index which includes, properly weighted, all of the conditions that will affect ignition under shock. In the region of the compacts such an index would take account chiefly of available hot spot sites*; in the approximately homogeneous region, it would indicate degree of homogeneity and compression (precompression will govern the heat generated by subsequent compression). In both regions, it would also

* For pure materials such sites would be expected to be voids (high stagnation temperatures from impacted spalls or jets) or particle/particle boundaries. But one material embedded in another produces another type of heterogeneity where shock interactions can create hot spots.

include, of course, the activation and reaction energies, factors that determine the ignitability of the particular explosive. If such an index could be used instead of % TMD, all of the curves of Fig. 5 should show a very sharp upward bend at the point where the material approaches non-detonability under LSGT conditions.

The explosive for which the most complete data are available on detonability and shock sensitivity is TNT. These data are assembled in Table 10 and have been used to construct the qualitative curves of Fig. 6 where shock sensitivity and critical diameter are shown as they would be expected to vary with the ignition index λ . The lower range of λ corresponds to the cold pressed charges; these TNT charges are porous in the literal sense of being permeable by liquids. The upper range of λ covers non-porous charges and runs from cast to single crystal and highly precompressed explosive. Porous charges can be converted to non-porous only dynamically. Otherwise, the method of preparation determines the permeability.

Fig. 6 has been drawn to emphasize that P_g and d_c vary in the same manner for a chemically homogeneous, approximately physically homogeneous, non-porous TNT charge. For porous charges, P_g and d_c vary in the same way for Group 2 materials, but in opposite directions for Group 1 materials as Fig. 6 illustrates with TNT. It seems reasonable to assume that the same factor is dominant in both measurements (P_g and d_c) in region (b) and that that factor is ignitability under shock. For TNT, the single crystal limit of region (b) is a voidless solid, and both ignition and propagation must be homogeneous processes. In region (a), on the other hand, we expect ignition to be a surface phenomenon, i.e., heterogeneous, whereas propagation can conceivably be by surface or bulk reaction or both. By the domination of the heterogeneous mechanisms in ignition and of the homogeneous in propagation, it is possible to have the opposite trends of P_g and d_c shown in region (a) for TNT.

Every explosive is expected to show a shock sensitivity curve like that of Fig. 6. However, the division between regions (a) and (b), which should occur at the same value of our ignition index λ , will occur at different % TMD and method of preparation. For example, it occurs in DNT just above 99% TMD (cold press) and somewhat below

TABLE 10

Shock Sensitivity and Detonability of TNT

	P_c (kbar)	d_c (mm)
Pressed 70-200 μ , 65% TNT, 25°C	10 ^a	8 ^b
Pressed 70-200 μ , 99% TNT, 25°C	23 ^a	42 ^b
Cast, 25°C	26-46 ^a	27 to >32 ^c
Liquid (81-03°C)	~110 ^d	68 ^e
Single Crystal 25°C	>110 ^f	>76 ^e

a. NOLTR 65-177

b. V. K. Bobolev, Dokl. Akad. Nauk SSSR 57, 789(1947) thru J.P.R.S: 4026.c. W. B. Cybulski, W. Payman, and D. W. Woodhead, Proc Roy Soc (London) 197A, 51(1949).d. W. B. Garn, J. Chem. Phys. 20, 819(1959).

e. A. N. Drem'in and V. S. Trofimov, Zhur. Prikl. Mek. i Tekh. Fiz. No. 1, 126(1964) through U. S. Dept. Commerce AD 615211, pp 205-216 (March 1964).

f. Higher P_c on crystal than on liquid is necessary to reach same shocked temperature. This takes account of lower initial temperature, lower compressibility, and lower specific heat of the crystal.g. It is assumed that single crystal will have $d_c \geq$ than that of any casting, and also that the confinement of the gap test produces an effective diameter of about 76 mm (effective diam for D in this case). A special TNT casting was prepared with very slow cooling of the melt. This casting was not detonable in the gap test. Hence the estimate for single crystal TNT.

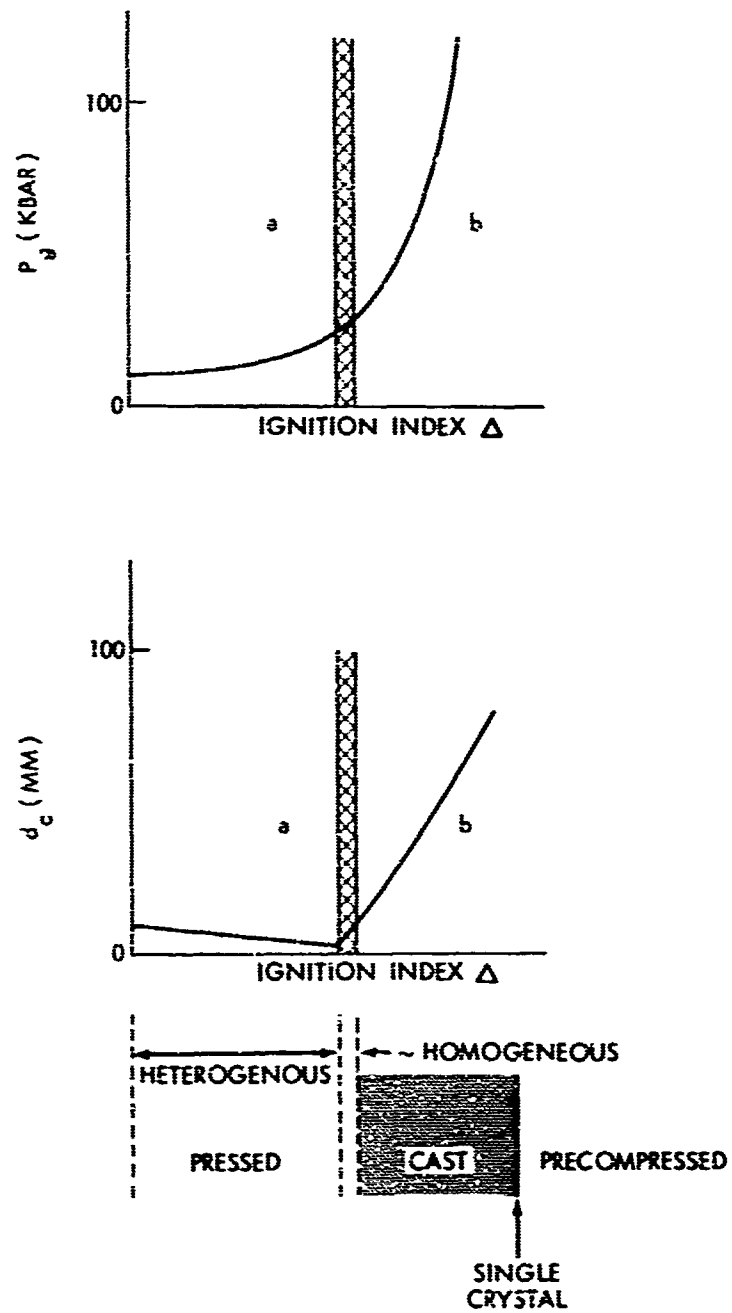


FIG. 6 DETONABILITY AND SHOCK SENSITIVITY OF TNT CHARGES

cast DNT. The general detonability curve is U shaped as we have recently shown⁹. Again, its minimum d_c should occur at the same value of the ignition index Δ . In fact, it occurs at high % TMD for Group 1 materials, at low % TMD for Group 2. Whether it will be possible to devise an ignition index capable of describing the behavior of all explosives remains, of course, an open question.

Although P_g and d_c show the same trends with Δ in region (b) for a pure compound, there seems no obvious relationship between P_g and d_c from compound to compound. This is illustrated by the data of Table 11 for three liquids and one single crystal, forms in which it is reasonable to expect all four explosives to be in the (b) region. Fig. 7 shows that all four of these materials require high initiation pressures P_1 as would be expected when bulk compression is the only mechanism for heating. Thus P_1 ranges from 82 to 112 kbar. But d_c varies from 2 to 68 mm and shows no obvious correlation with P_1 . In the more complex case of voidless but chemically (and hence physically) heterogeneous charges, e.g., aluminized, the trends in P_g and d_c with Al content can be the same (plastisol propellant) or opposite (TNT). A great deal more work is needed to clarify factors affecting both P_g and d_c .

SUMMARY

1. DNT shows Group 1 explosive behavior by both detonation velocity pattern and detonability limit curve.
2. At 98-99% TMD, it appears to be approaching a dead press limit in the LSGT. Hence a reversal in its detonability curve is probable at high compaction.
3. The infinite diameter detonation velocity is

$$D_1 \text{ (mm/usec)} = 1.64 - 2.913p_0$$

This is based on too few experiments to be highly reliable, however.

4. The detonability curve of (5-10 μ) DNT lies closest to that of NQ-n among explosives which have been studied.
5. The shock sensitivity curve of DNT lies between that for DATB (production quality) and TATB.

TABLE 11

Measurements of d_c * Initiation Pressure (P_i) on Homogeneous Explosives

Material	Form	ρ_c , g/cc	P_i (kbar)	d_c (mm)
RM	1, 20°C	1.13	82 ^a	18 ^b
TNT	1, 81-83°C	1.47	110 ^c	68 ^c
NG	1, 20°C	1.59	85 ^d	2.1 ^e
PETN	single crystal	1.77	112 ^f	8.5 \times d_c - 19

- a. A. W. Campbell, W. C. Davis, and J. R. Travis, Phys. Fluids 4, 498(1961)
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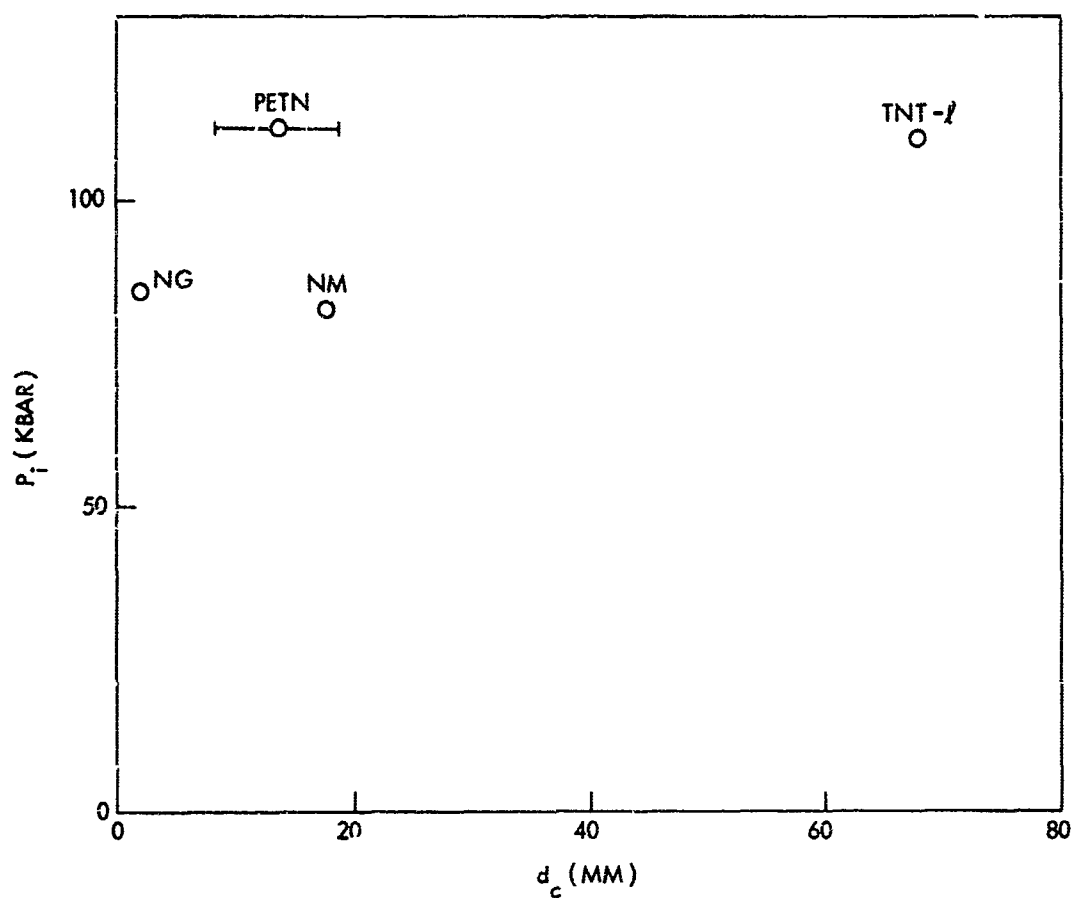


FIG. 7 INITIATION PRESSURE VS. CRITICAL DIAMETER FOR FOUR PURE HOMOGENEOUS EXPLOSIVES

ACKNOWLEDGMENT

We wish to thank Dr. K. G. Shipp for re-precipitating the commercial DNT to prepare batch X628 of the fine material.

NOTE ADDED IN PRESS: Corrections made to the measured detonation velocity are based on two assumptions: spherical expansion of the detonation front with distance of travel and an increase in the radius of curvature of the front passing from the booster to an acceptor of lower detonation velocity (e.g., DNT).⁶ In very recent work we have found a number of situations for which these assumptions are incorrect. Hence we do not feel that the corrections made to the measured D values of this report can be justified without an additional study of the detonation wave profiles in DNT. Both the "corrected" and uncorrected data lead to the same conclusions except for a small change in Eq. (1). This becomes

$$D_1 \text{ (mm/}\mu\text{sec)} = 1.96 + 2.913\rho_0$$

when derived from the measured D values.

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APPENDIX

Supplementary Data

Table A1 contains the Ro-Tap Sieve Analyses of DNT X587 and N137. Table A2 contains all the pin measurements which were summarized in Table 3 of the text.

TABLE A1

Ro-Tap Sieve Analyses of DNT
(100g samples)

	<u>Lot X587</u>						
Screen No.	60	100	140	200	230	270	Pan
" opening, μ	250	149	105	74	62	53	--
Retained, Run 1, g	24.4	31.5	16.4	13.6	6.1	5.2	2.1
Retained, Run 2, g	23.4	30.1	16.9	13.6	6.8	5.5	3.6

By microscopic examination, this material consisted of chunky cylinders with l/d of 4 to 7.

	<u>Lot N137</u>					
Screen No.	10	14	18	30	60	Pan
" opening, μ	2000	1410	1000	590	250	--
Retained, g	0.6	0.5	2.1	6.8	71.7	18.0

This material too was in the form of chunky cylinders with and l/d of 2 the most common.

TABLE A2
Details of Measurements Summarized in Table 3

Distance between Pins	Pin	Shot #1		Shot #2		Shot #4	
		Δt μsec	Vel. $\text{mm}/\mu\text{sec}$	Δt μsec	Vel. $\text{mm}/\mu\text{sec}$	Δt μsec	Vel. $\text{mm}/\mu\text{sec}$
in.*	1	0	0	0	0	0	0
2.0	2	11.926	4.260	11.575	4.388	9.404	5.402
2.0	3	11.612	4.374	12.766	3.980	8.507	5.972
1.0	4	6.554	3.876	6.626	3.834	4.376	5.804
1.0	5	6.749	3.764	6.914	3.674	4.425	5.740
1.0	6	6.684	3.800	6.647	3.822	4.188	6.064
1.0	7	6.734	3.772	6.774	3.750	4.277	5.938
1.0	8	6.768	3.752	6.820	3.724	4.366	5.818
1.0	9	6.649	3.820	6.769	3.752	4.254	5.970
1.0	10	6.652	3.818	6.498	3.908	4.292	5.918
		Av. 3.80		Av. 3.78		Av. 5.89	

Type of Pins
Precision Research** Precision Research**

EQ & G**

booster Tetryl 2"

DNT X587

* First pin 12.7 mm from booster surface

** Both types of ionization pins were 32 mil. In the EQ & G, No. CA 1040, the insulation was teflon; in the Precision pin, the insulator is air. The latter pin showed a higher frequency of failures when tested statically.

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DOCUMENT CONTROL DATA - R&D		
<small>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</small>		
1 ORIGINATING ACTIVITY (Corporate author) U. S. Naval Ordnance Laboratory White Oak, Silver Spring, Md.		2a REPORT SECURITY CLASSIFICATION UNCLASSIFIED
		2b CR, JP
3 REPORT TITLE Explosive Behavior of Dinitrotoluene		
4 DESCRIPTIVE NOTES (Type of report and inclusive dates)		
5 AUTHOR(S) (Last name, first name, initial) Price, D.; Erkman, J. O.; Clairmont, Jr., A. R.; and Edwards, D. J.		
6. REPORT DATE 10 July 1969	7a. TOTAL NO. OF PAGES 47	7b. NO. OF REFS 15
8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S) NOLTR 69-92	
A. PROJECT NO. MAT 03L 000/R011 01 01 C. TASK 033 102 F009 06 01	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
10 AVAILABILITY/LIMITATION NOTICES This document has been approved for public release and sale, its distribution is unlimited.		
11 SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Naval Ordnance Systems Command Washington, D. C.	
13 ABSTRACT DNT shows Group 1 explosive behavior although it can be dead-pressed moderately easily. Its infinite diameter detonation velocity is approximated by $D_1 \text{ (mm/}\mu\text{sec)} = 1.84 + 2.913 p_0$ Its detonability and shock sensitivity are, respectively, near those of high bulk density nitroguanidine and DATB. A review of factors affecting detonability and sensitivity of a chemically homogeneous explosive is also presented.		

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14. KEY WORDS	LINK A		LINK B		LINK C	
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